

# GC-MS/MS Determination of Pesticide Residues in Fruit Using the Xevo TQ-GC

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## APPLICATION BENEFITS

Provides a multiresidue GC-MS/MS method for the determination of pesticide residues in fruit commodities, with extraction using the QuEChERS workflow, suitable for monitoring for MRL compliance. This method which was developed on Waters™ Xevo™ TQ-GC provides fit-for-purpose performance in terms of sensitivity, linearity, and robustness.

## WATERS SOLUTIONS

[Xevo TQ-GC](#)

[MassLynx™ MS Software](#)

[TargetLynx™ XS Application Manager](#)

[Quanpedia™ Database](#)

[DisQuE™ QuEChERS CEN Method Sample Preparation Pouches](#)

[DisQuE QuEChERS Dispersive SPE Tubes](#)

## KEYWORDS

GC-MS/MS, GC, pesticides, residue analysis, MRL, QuEChERS, SANTE guidelines

## INTRODUCTION

Pesticide residues remain a priority on the list of food safety concerns. As a result, laboratories are required to create analytical methods capable of screening the maximum amount of compounds, using a minimal number of methods, while ensuring sample turnaround times are met. The majority of countries have established clearly defined regulations<sup>1</sup> relating to pesticide residues, with legislation imposing Maximum Residue Limits (MRLs)<sup>2</sup> levels for different food commodities. To meet these criteria, laboratories require analytical techniques that are sensitive, accurate, and robust.

Multiresidue analysis is challenging due to the varying matrix complexity of different food commodities and the requirement for low part per billion (ppb or mg/kg) detection levels to achieve MRL compliance for a diverse range of pesticides. Currently there are in excess of 1000 pesticides known to be in use, and laboratories are continually under pressure to increase the scope of analytical methods employed for routine monitoring purposes. Various technologies are used to meet these challenges with the most common being liquid chromatography (LC) and gas chromatography (GC) coupled to tandem quadrupole mass spectrometry (MS/MS), which allows laboratories to cover a wide range of compounds as required by legislation.<sup>3</sup>

In this application note we provide example performance data from Waters Xevo TQ-GC System for pesticide residues in two different commodities. Samples were extracted by the QuEChERS CEN method and cleaned-up by dispersive solid phase extraction (d.SPE), following the protocol described in a EURL-FV multiresidue method, using QuEChERS for fruits and vegetables.<sup>4</sup>

## EXPERIMENTAL

### Sample preparation and extraction

Homogenized organic apple was extracted using the QuEChERS method as shown in Figure 1. Organic raisin was first rehydrated with LCMS water and then the equivalent to 5 g of sample was taken for QuEChERS extraction. The supernatant from the QuEChERS extracts were then cleaned-up by d.SPE tubes which contained 25 mg of primary secondary amine (PSA) sorbent and 150 mg MgSO<sub>4</sub>, per 1 mL of sample extract. Samples were then evaporated and reconstituted in ethyl acetate, post spiked with the pesticide mix, and analyzed using the gas chromatography, mass spectrometry method highlighted below. Analyte extraction recovery was not assessed during this work, QuEChERS is a well established sample extraction method for pesticides in food and the aim of this work was to assess the GC-MS/MS method performance only.

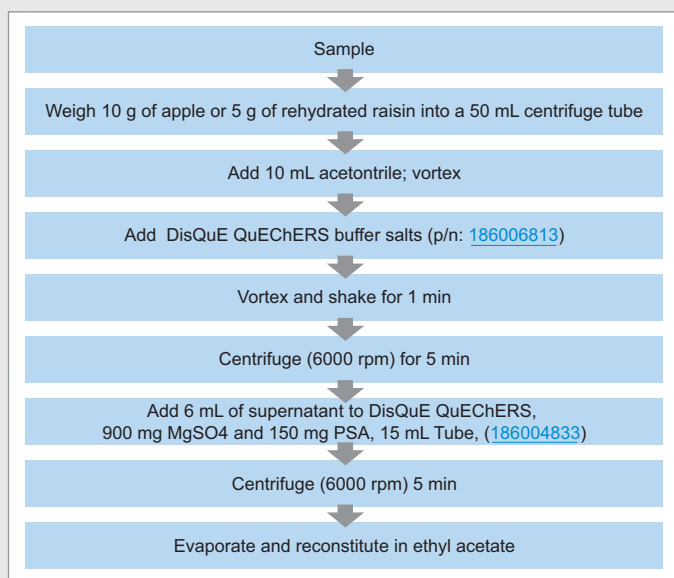


Figure 1. Sample preparation and QuEChERS workflow used to prepare the samples.

The performance of the GC-MS/MS step of the method was assessed using SANTE guidelines<sup>5</sup> for 150 pesticides. Solutions of matrix-matched standards were prepared over the range 0.001 to 0.050 mg/kg (1.0 to 50.0 ppb in vial concentration) in apple, and 0.002 to 0.100 mg/kg (1.0 to 50.0 ppb in vial concentration) in raisin. Replicate injections at three concentration levels were run between bracketed calibration curves to assess the performance of the method. An internal standard (triphenylphosphate) was added to all samples prior to the analysis to correct for any injection variability which may have occurred.

### GC conditions

GC column:	Rxi-5MS 30 m x 0.25 mm id x 0.25 µm (Restek)
Carrier gas:	Helium
Gas flow rate:	1.4 mL/min
Injection type:	Pulsed splitless
Inlet temp.:	280 °C
Pulse time:	1.10 min
Pulse pressure:	170 kPa
Purge flow:	30 mL/min
Septum purge flow:	3 mL/min
Inlet liner:	Gooseneck splitless liner 4 mm x 6.5 x 78.5 (Restek)
Wash solvent:	Hexane (A) and ethyl acetate (B)
Oven program:	91 °C (hold 1.0 min) to 330 °C at 8.5 °C/min and hold for 5 min, run
Run time:	34.12 min
Injection volume:	1 µL

### MS conditions

MS system:	Xevo TQ-GC
Software:	MassLynx v4.2
Ionization mode:	El <sup>+</sup> , 70eV
Source temp.:	250 °C
GC interface:	320 °C
MRM:	All transitions were imported from Waters Quanpedia Database, and further information can be obtained in Waters technology brief no.: <a href="#">720006248en</a> . IntelliStart™ Custom Resolution settings were used.

## RESULTS AND DISCUSSION

Method development or method transfer on a new GC-MS/MS system can be time consuming, requiring parameters such as MRM transitions, collision energies, chromatography conditions, and processing methods to be optimized. To speed up this process, Quanpedia Database was used to automatically establish these parameters with minimal manual optimization required. An example of the Quanpedia workflow is shown in Figure 2.

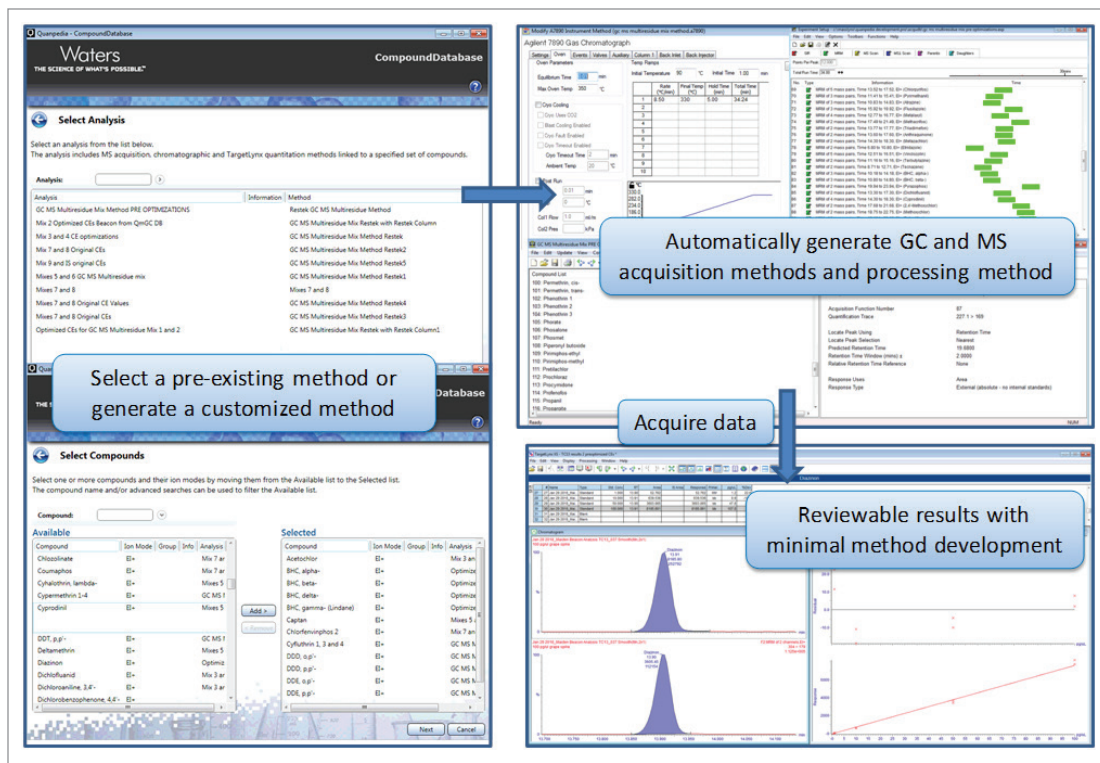


Figure 2. Example workflow using Quanpedia to generate a new pesticide multiresidue analysis and Targetlynx XS processing method for routine analysis.

The linearity of the method was assessed using bracketed matrix-matched calibration curves, which were internal standard corrected. Figure 3 shows the calibration curves for alpha-BHC in both organic apple and raisin.

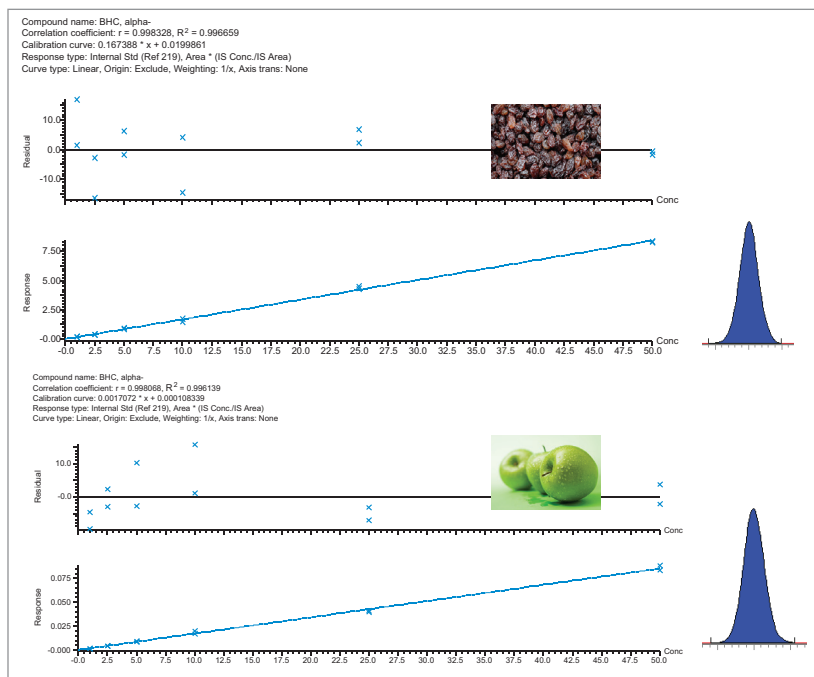


Figure 3. Matrix matched calibration curves at 1 ng/mL to 50 ng/mL, and 0.010 mg/kg chromatograms for alpha-BHC in organic raisin and apple.

The linearity of response and calibration range in organic raisin for all 150 pesticides assessed in this study are shown in Figure 4. The calibration curve data for all 150 compounds can be found in Appendix 1. The concentration levels take into account that only 5 grams of rehydrated raisin sample was taken for extraction. All compounds gave excellent linear response and only one compound, trans-nanochlor, gave a linear response <0.990. All residuals (back calculated concentrations) were within the 20% tolerance of the SANTE guidelines, with calibration ranges between either 0.002 mg/kg or 0.005 mg/kg to 0.100 mg/kg.

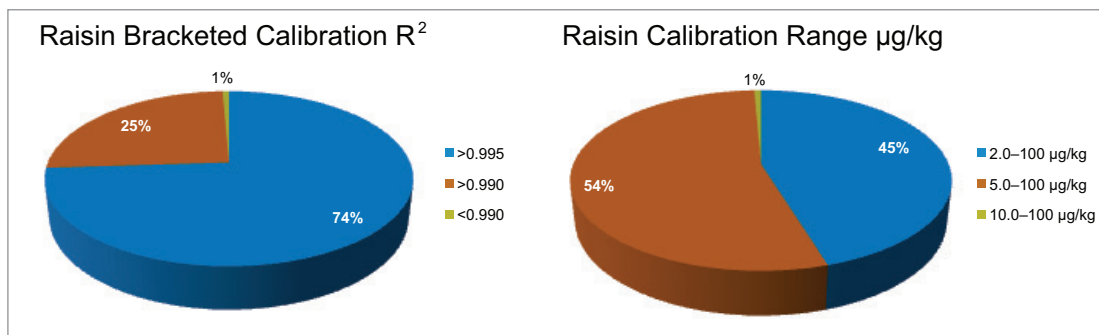


Figure 4. Matrix-matched bracketed calibration data for 150 pesticides spiked into QuEChERS extracted organic raisin.

Replicate (n=6) injections were run for three levels, 0.005 mg/kg, 0.010 mg/kg, and 0.020 mg/kg in each matrix. The calculated mean concentrations and precision for representative pesticides in organic raisin are shown in Figures 5 and 6.

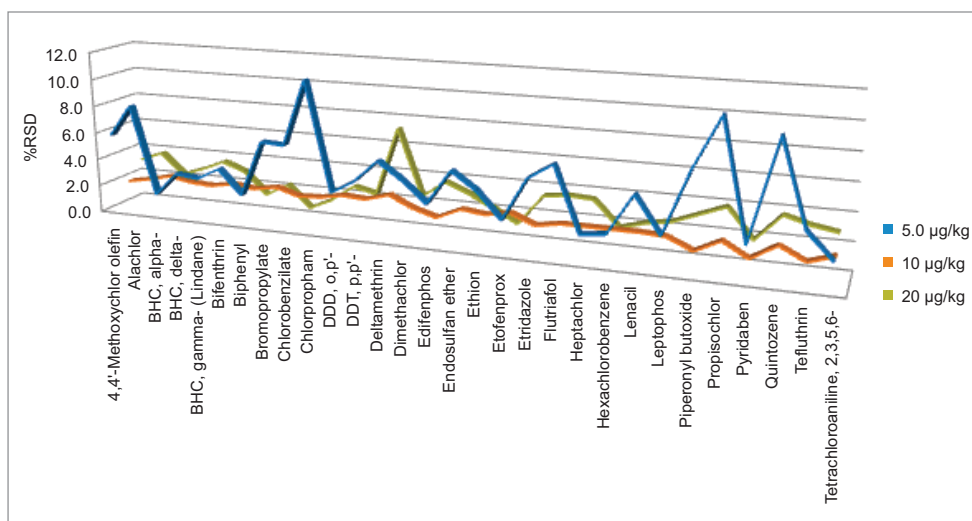


Figure 5. Repeatability (%RSD) data for representative pesticides in organic raisin using matrix-matched QC points (n=6) at 0.005 mg/kg, 0.010 mg/kg, and 0.020 mg/kg.

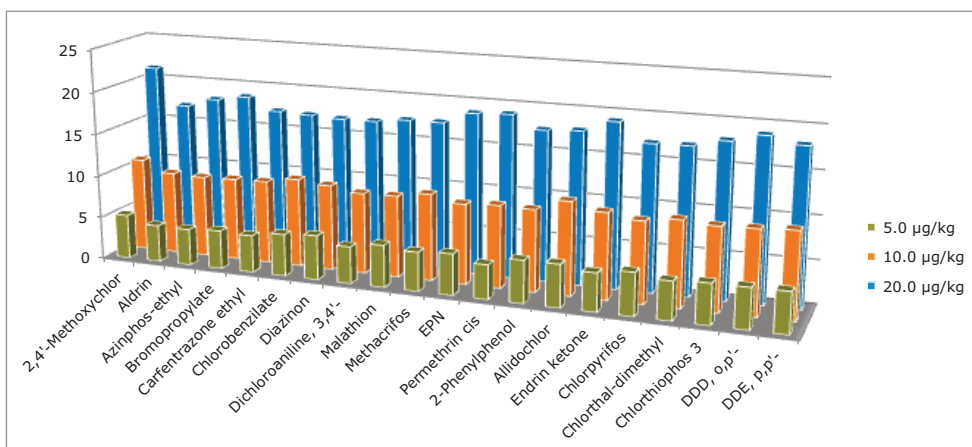


Figure 6. Calculated mean concentration data for representative pesticides in matrix-matched QC points (n=6) for organic raisin at 0.005 mg/kg, 0.010 mg/kg, and 0.020 mg/kg.

Ion ratios and retention times from the matrix-matched standards agreed well with the reference values and most were within the required tolerances ( $\pm 30\%$  and  $\pm 0.1$  min, respectively). An example of the ion ratios given by each of the QC levels for deltamethrin in organic raisin and apple can be seen in Figure 7.

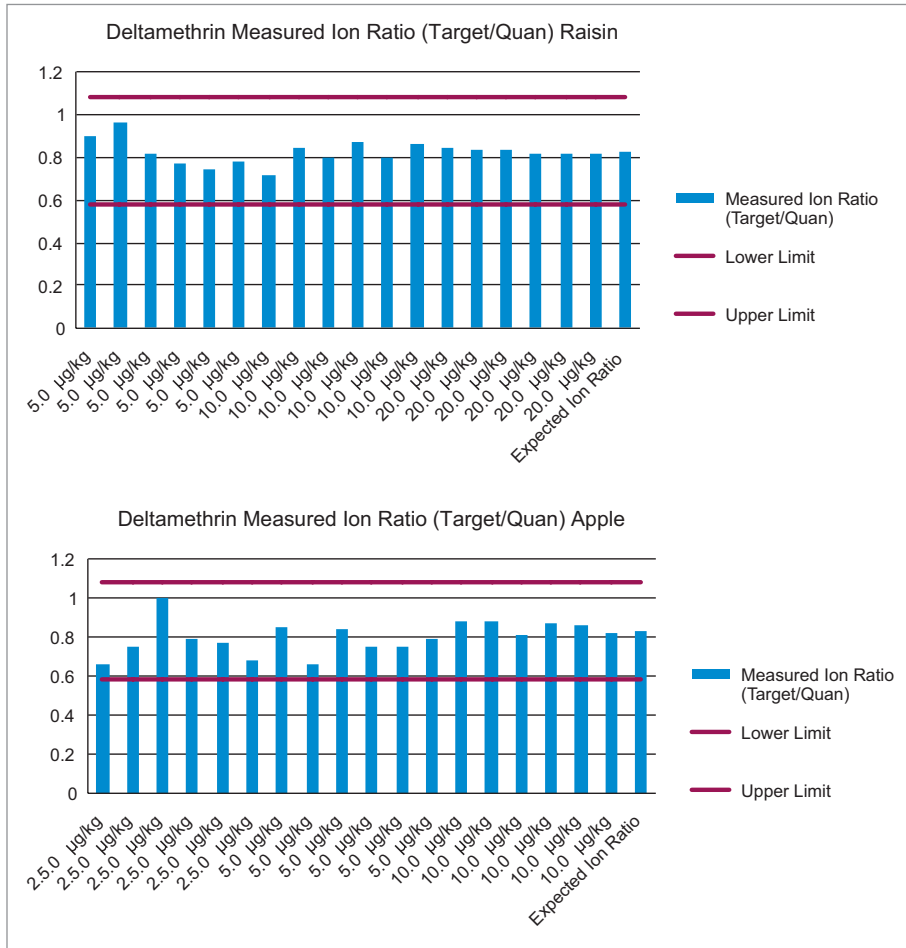


Figure 7. Ion ratios for the three QC levels of deltamethrin in A. raisin, and B. apple.

## CONCLUSIONS

The goal of this study was to evaluate the performance of the Xevo TQ-GC for the determination of pesticide residues in fruit commodities prepared by QuEChERS sample preparation methodology. The Xevo TQ-GC provided excellent, fit-for-purpose performance in terms of linearity and calibration range for both organic raisin and apple. The trueness and precision of the GC-MS/MS method determined at three QC levels was found to be acceptable with the representative compounds shown, giving %RSD <10%. Overall the performance data indicate that the Xevo TQ-GC, when used in combination with an established extraction protocol such as QuEChERS, is suitable for checking MRL/tolerance compliance in routine laboratory testing.

## References

1. European Union (2009) Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 Concerning the Placing of Plant Protection Products on the Market and Repealing Council Directives 79/117/EEC and 91/414/EEC [[Online](#)].
2. European Commission (2016) EU Pesticide Database [[Online](#)].
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4. European Union Reference Laboratory – Fruits and Vegetables, 'Multiresidue Method Using QuEChERS Followed by GC-QqQ/MS/MS and LC-QqQ/MS/MS for Fruits and Vegetables' [[Online](#)].
5. European Union (2017). Document No. SANTE 11813/2017. Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed.

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## Appendix

*Pesticides assessed in this study and calibration results for organic raisin.*

Name	Coeff. of determination (Raisin)	Calibration range µg/kg (Raisin)
2,4'-Methoxychlor	0.999	2.0-100
2-Phenylphenol	0.997	2.0-100
4,4'-Methoxychlor olefin	0.997 (2nd order)	2.0-100
Acetochlor	0.997	2.0-100
Acrinathrin	0.993	5.0-100
Alachlor	0.998	5.0-100
Aldrin	0.996	2.0-100
Atrazine	0.996	5.0-100
Azinphos-ethyl	0.991	5.0-100
Benfluralin	0.997	5.0-100
BHC, alpha-	0.997	2.0-100
BHC, beta-	0.995	2.0-100
BHC, delta-	0.997	2.0-100
BHC, gamma- (Lindane)	0.995	2.0-100
Bifenthrin	0.998	5.0-100
Biphenyl	0.995	2.0-100
Bromfenvinphos	0.996	5.0-100
Bromfenvinphos-methyl	0.996	5.0-100
Bromophos-methyl	0.997	5.0-100
Bromopropylate	0.994	2.0-100
Bupirimate	0.995	2.0-100
Carfentrazone ethyl	0.995	5.0-100
Chlordane, trans-	0.994	5.0-100
Chlorfenson	0.994	5.0-100
Chlorobenzilate	0.996	2.0-100
Chloroneb	0.995	2.0-100
Chlorpropham	0.996	2.0-100
Chlorpyrifos	0.995	5.0-100
Chlorpyrifos-methyl	0.995	5.0-100
Chlorthal-dimethyl	0.997	2.0-100
Chlorthiophos 3	0.998	5.0-100
Chlozolate	0.995	5.0-100
Clomazone	0.996	2.0-100
Coumaphos	0.991	5.0-100
Cyfluthrin I	0.995	5.0-100
Cyfluthrin II	0.994	5.0-100
Cyfluthrin III	0.991	5.0-100
Cyfluthrin IV	0.990	5.0-100
Cyfluthrin I-IV	N/A	5.0-100
Cyhalothrin, lambda-	0.994	2.0-100
Cypermethrin I	0.997	5.0-100
Cypermethrin II	0.991	5.0-100
Cypermethrin III	0.990	5.0-100
Cypermethrin IV	0.993	5.0-100
Cypermethrin Peaks I-IV	N/A	5.0-100
Cyprodinil	0.995	5.0-100
DDD, o,p'-	0.999	2.0-100
DDD, p,p'-	0.996	2.0-100

DDE, p,p'-	0.995	2.0-100
DDT, o,p'-	0.995	2.0-100
DDT, p,p'-	0.998	5.0 -100
Deltamethrin	0.996	5.0-100
Diallate 1	0.997	2.0-100
Diallate 2	0.995	2.0-100
Diazinon	0.997	5.0-100
Dichloroaniline, 3,4'-	0.997	5.0-100
Dichlorobenzophenone, 4,4'-	0.995	5.0-100
Diclobenil	0.995	2.0-100
Dicloran	0.996	5.0-100
Dimethachlor	0.996	2.0-100
Edifenphos	0.995	5.0-100
Endosulfan ether	0.996	2.0-100
Endosulfan I	0.994	10.0-100
Endosulfan II	0.995	5.0-100
Endosulfan sulfate	0.998	5.0-100
Endrin	0.995	5.0-100
Endrin Aldehyde	0.993	2.0-100
Endrin ketone	0.993	2.0-100
Enthalfuralin	0.992	5.0-100
EPN	0.990	5.0-100
Ethion	0.996	5.0-100
Etofenprox	0.997	2.0-100
Etridazole	0.996	2.0-100
Fenarimol	0.995	2.0-100
Fenchlorphos	0.997	5.0-100
Fenitrothion	0.994	5.0-100
Fenson	0.995	2.0-100
Fenvalerate 1	0.993	2.0-100
Fluchloralin	0.994	5.0-100
Flucythrinate 1	0.992	2.0-100
Flucythrinate 2	0.992	2.0-100
Fludioxonil	0.995	5.0-100
Fluquinconazole	0.997	5.0-100
Fluridone	0.993	5.0-100
Flutoanil	0.997	5.0-100
Flutriafol	0.998	5.0-100
Fonofos	0.996	2.0-100
Heptachlor	0.996	2.0-100
Hexachlorobenzene	0.995	2.0-100
Hexazinone	0.990	5.0-100
Iodofenfos	0.993	5.0-100
Isazophos	0.996	5.0-100
Isodrin	0.995	2.0-100
Isopropalin	0.997	5.0-100
Lenacil	0.992	5.0-100
Leptophos	0.996	5.0-100
Linuron	0.994	5.0-100
Malathion	0.996	2.0-100
Metalaxyl	0.995	5.0-100
Metazachlor	0.997	2.0-100
Methacrifos	0.996	2.0-100
Methoxychlor	0.998	2.0-100
Methyl parathion	0.991	5.0-100



Metolachlor	0.997	2.0-100
Mevinphos	0.996	5.0-100
Mirex	0.997	2.0-100
Myclobutanil	0.995	2.0-100
Nanochlor, trans-	0.986	5.0-100
Nitrofen	0.996	5.0-100
Nonachlor, cis-	0.997	5.0-100
Norflurazon	0.995	5.0-100
Oxadiazon	0.995	5.0-100
Paclobutrazol	0.992	5.0-100
Pebulate	0.997	2.0-100
Penconazole	0.997	2.0-100
Pentachloroaniline	0.994	5.0-100
Pentachloroanisole	0.995	2.0-100
Pentachlorobenzene	0.995	2.0-100
Pentachlorobenzonitrile	0.996	5.0-100
Pentachlorothioanisole	0.996	5.0-100
Permethrin cis	0.996	2.0-100
Permethrin trans	0.995	5.0-100
Phosalone	0.994	5.0-100
Phosmet	0.996	2.0-100
Piperonyl butoxide	0.995	2.0-100
Pirimiphos-methyl	0.997	5.0-100
Pretilachlor	0.999	2.0-100
Procymidone	0.998	5.0-100
Propachlor	0.997	2.0-100
Propisochlor	0.996	5.0-100
Propyzamide	0.999	5.0-100
Prothiofos	0.997	5.0-100
Pyraclofos	0.991	5.0-100
Pyrazophos	0.993	5.0-100
Pyridaben	0.995	5.0-100
Pyridaphenthion	0.993	2.0-100
Pyrimethanil	0.994	5.0-100
Pyriproxyfen	0.997	2.0-100
Quinalphos	0.995	5.0-100
Quintozene	0.998	2.0-100
Sulfotep	0.997	2.0-100
Tebuconazole	0.991	2.0-100
Tebufenpyrad	0.999	2.0-100
Tecnazene	0.994	5.0-100
Tefluthrin	0.996	2.0-100
Tetrachloroaniline, 2,3,5,6-	0.996	2.0-100
Tetradifon	0.997	2.0-100
Tetrahydrophthalimide	0.996	2.0-100
Tolclofos-methyl	0.997	2.0-100
Triallate	0.996	5.0-100
Triazophos	0.994	5.0-100
Trifluralin	0.997	5.0-100
Vinclozolin	0.995	2.0-100